present state of vagueness on the subject of "promoters," because they establish for one particular case—

(i) The connection between optimum concentration of promoter and amount of *catalyst*, not of organic compound;

(ii) The transformation of the action from one typical of the presence of catalyst poisons (in absence of carbonate) to one almost of the usual type prevailing in the absence of any catalyst poison (in presence of carbonate);

(iii) The "acceleration" of the action in presence of the "promoter" is in this case not a true acceleration, but the removal of a retardation; this leaves the catalyst itself free to behave more normally.

A Study of Catalytic Actions at Solid Surfaces. Part IX.—*The Action of Copper in Promoting the Activity of Nickel Catalyst.*

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One of the most interesting cases of promoter action is that in which a mixture of two substances, each of which functions as a catalyst for the same action, shows greater activity than either constituent alone.

Thus in the synthesis of ammonia an iron-molybdenum catalyst is stated to afford greater yields of ammonia than is given by either of the metals alone.* Again, the production of formaldehyde from methyl alcohol and air was found by Hochstetter to be more effectively performed in presence of a silver-copper alloy than by either silver or copper alone.† Carbon monoxide is oxidised more efficiently in presence of certain mixtures of oxides, for example "hopcalite," than in presence of the constituent oxides (manganese and copper oxides).‡

A somewhat different case concerns the simultaneous action of two catalysts exerting different functions.

Camphor can be converted to camphane by catalytic reduction over nickel to borneol, dehydration of the latter to camphene over alumina, and hydrogenation of camphene to camphane. The hydrogenation proceeds readily at or below 200° C., but the dehydration in presence of alumina takes place at 350° C. or above. If, however, a mixed nickel-alumina catalyst be prepared, the whole sequence of changes may be carried out in one step, and at 200° C.*

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* 'Badische Anilin und Soda Fabrik,' German Patent No. 5833 (1911).

† U.S.A. Patents 1100076, 1110289.

‡ Lamb, Bray and Frazer, 'J. Ind. Eng. Chem.,' vol. 12, p. 213 (1920).

We have observed the same phenomenon in the hydrogenation of phenol vapour over a nickel-alumina mixture at 180° C., when considerable proportions of cyclohexane are produced by dehydration and reduction of cyclohexanol; the latter requires, however, a temperature of 350° C. before dehydration to cyclohexane occurs in the presence of alumina alone.

To these instances may be added the subject of the present paper, namely, the behaviour of mixed copper-nickel catalysts in hydrogenation. Dewar and Liebmann† stated that mixed copper-nickel catalysts were of higher activity than nickel itself, and could be prepared by reduction at the very low temperature of 170–180° C.

We would emphasize here the importance of an adequate standard of activity; before committing ourselves to the statement that a mixed catalyst is more active than one of its constituents, it is necessary to consider under what conditions its activity is measured. Thus, in the case of nickel, Dewar and Liebmann's statement will undoubtedly hold if the comparison is made between a mixed copper-nickel preparation and pure finely divided nickel alone. But it is common knowledge that the full activity of nickel is not displayed unless it is adequately distributed on a support; we have indicated in a previous communication‡ some of the conditions determined by the surface-area of the catalyst. If the comparison is made between nickel thus distributed to display its maximum efficiency§ and mixed copper-nickel similarly mounted, we have never found the activity of the usual type of reduced nickel to be surpassed by the latter.

The interesting point is, that by employing supported copper-nickel compounds prepared in a suitable manner it is possible to obtain production of free nickel by exposure to hydrogen at 170–180° C., whereas similarly supported nickel compounds alone are not reduced by hydrogen below 300° C., and not rapidly below 350–400° C.

Detailed investigation of mixed copper-nickel catalysts has shown that in order to obtain the reduction of the nickel at this relatively low temperature the copper and nickel must, prior to reduction, be intimately and chemically associated with each other.

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* Ipatieff, 'Ber.,' vol. 45, p. 3205 (1912).

† British Patents 12981/1913 and 15668/1914.

‡ Part VI of this series, 'Roy. Soc. Proc.,' A, vol. 99, pp. 490–495 (1921).

§ We may point out, however, that although distribution over a large surface and reduction of apparent volume undoubtedly have a preponderating influence, we have no definite knowledge at present as to whether the constituents of the more suitable supports also exert a specific activating ("promoting") effect on the nickel. In the absence of positive proof of the latter point, we prefer to compare catalysts mounted on a support which is known to give a good surface distribution of the metal.

In the first place, simple grinding together of nickel and copper compounds is of little use; to secure any effect the latter must be precipitated together before reduction.

This conclusion is based on some experiments in which various mixtures of copper and nickel carbonates were suspended in highly-refined cotton-seed oil and treated with hydrogen at 180° C. for 3 hours. The original oil absorbed 108·7 per cent. of its weight of iodine and the percentage absorption of iodine (iodine number) of the treated oils indicates the extent to which hydrogenation had proceeded.

The experiments were made both with the simple carbonates and the same carbonates precipitated in the customary manner on kieselguhr, 5 grm. of each preparation being used in conjunction with 150 grm. of the purified cotton-seed oil:—

	Iodine absorption of product after 3 hours at 180° C.	
	Carbonates alone.	Carbonates on kieselguhr.
Copper carbonate alone	108·0	99·0
Copper carbonate and nickel carbonate intimately mixed by grinding	100·1	97·2
Copper and nickel carbonates precipitated together from solution	2·5	3·1

It was found that whilst, of course, the copper was completely reduced to the metallic state in all cases, the nickel was only reduced in the latter case (co-precipitation), and then only to the extent of about 10 per cent. of the total nickel present. This was confirmed by examination of the products obtained by reduction of the copper-nickel carbonates in hydrogen alone at 170°–180° C. As a rule, only 7–8 per cent. of the nickel present was found to be in the metallic state, one or two exceptional cases showing up to 12 and 15 per cent.

Further experiments with co-precipitated copper and nickel carbonates on kieselguhr were marked by several failures to obtain more than a very little catalytic activity in the product. The cause of these variations was traced by means of a somewhat involved series of experiments, which we need not give in detail, to slight modifications in the precipitation of the mixed carbonates. The final conclusion reached was that, in order to obtain the best activity, a somewhat incomplete precipitation of the copper by alkaline carbonate was essential, for it was found that, as the filtrates from the preparation were more deeply coloured, so the activity increased. Parallel with this, it was observed that the colour of the prepared catalyst (in the form of precipitated carbonate) varied from brown, or grey in an inactive preparation, to pale blue, or greenish-blue, in the more active catalysts.

This may be illustrated by a few figures showing the melting-point of cotton-seed oil after hydrogenation for 3 hours at 180° C., under comparable conditions, with the same weight of prepared copper-nickel carbonate of varying appearance.

Copper-nickel carbonate on kieselguhr.		Melting-point of cotton-seed oil after 3 hours' treatment.
Colour of preparation.	Colour of alkaline filtrates.	
Brown	Colourless	Liquid
Drab	"	"
Greenish-grey	"	50°
Pale greenish-blue	Pale blue	56°
Pale blue	Deep blue	61–62° (saturated)

The various basic copper carbonates which it was evident were in question were then studied in the light of Pickering's classical work on the complex carbonates of copper,* and it was found that a very close connection existed between the precipitates giving rise to active catalysts, and the class of compounds termed by Pickering α-cupricarbonates. The latter, formulated as $Na_2Cu(CO_3)_2$, are characterised by solubility in alkaline carbonate solutions to an intense blue solution, which contains electro-negative copper and oxidises glucose, whilst in caustic alkali solutions they yield dark violet-blue liquids, which, in addition to the above reactions, also dissolve cellulose, and, on standing deposit malachite or other basic carbonate. On the other hand, basic carbonates of copper alone are insoluble in both mild and caustic alkali if the molecular ratio of copper oxide to carbon dioxide is 3 : 1, or over, whilst if it is less than 3 : 1 they are insoluble in alkaline carbonate, but give the deep violet-blue solution with aqueous caustic soda.

The various preparations which we had made (some fifteen in all) were triturated with cold 10-per-cent. sodium carbonate and 10-per-cent. caustic potash solutions, allowed to settle, and the clear liquor decanted and examined, when it was found that an exact correlation existed between Pickering's criteria for α-cupricarbonates, and the preparations which yielded the more active catalysts on reduction. The data obtained for the five preparations quoted in the preceding Table will serve to illustrate this:—

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* 'Chem. Soc. Trans.,' vol. 95, p. 1409 (1909).

Colour of preparation.	Melting-point of cotton-seed oil after 3 hours' treatment.	Aqueous extract of preparation with	
		10 per cent. sodium carbonate.	10 per cent. caustic potash.
Brown	Liquid	Colourless, no copper present	Pale yellow, trace of electronegative copper.
Drab	,,	Pale yellow, no copper present	Electronegative copper.
Greenish-grey	50°	Slight pale green, trace of electronegative copper	Transitory violet-blue, oxidised glucose.
Pale greenish-blue	56°	Pale bluish-green, contained electronegative copper, oxidised glucose	Deep violet-blue, depositing deep-blue crystals on standing; oxidised glucose and united with cellulose.
Pale blue	61–62° (saturated)		

The parallelism between activity and the tests for cupricarbonates is exact, and it may legitimately be inferred that the power of reducing nickel carbonate at 180° C. is connected in some way with the presence of electronegative copper in the precipitated material.

The substance present in the washed and dried preparation is clearly not sodium cupricarbonate, which is unstable in dilute solution; it seems more probable that under controlled conditions of precipitation the latter salt, formed from the copper salt and sodium carbonate, has given rise to a nickel cupricarbonate, which is likewise not very stable and may easily be resolved into a mixture of nickel carbonate and basic copper carbonates.

Thus we are led to the view that to obtain any degree of catalytic activity the nickel and copper must not simply be intimately mixed by being precipitated together, but must also be contained in the same complex carbonate molecule.

When at least a portion of the nickel present is thus combined with copper, it is reduced at 180° C., and is ready for service as a catalyst of hydrogenation. We venture to suggest that the apparently low temperature of reduction may be simply explained if the above evidence of a nickel cupricarbonate formation is accepted: the reduction of copper carbonate or oxide is strongly exothermic, so much so that, for example, it is very difficult to maintain the temperature of a compact mass of copper oxide below 180° C. once reduction has set in. This heat is equally liberated, of course, as the copper in each cupricarbonate molecule is reduced, and although it is rapidly conducted away, it is obvious that at the moment of reduction the temperature of the molecule itself is momentarily raised to a considerable degree, and consequently the actual temperature of reduction of the nickel combined in the same molecule as the copper must be considerably above 180° C. We believe that the mechanism of the reduction is simply that the necessary local heat to provide a sufficiently high temperature for the reduction of the nickel is forthcoming from the reduction of the copper, providing that the latter is in sufficiently close proximity to the nickel—and our results indicate that nothing short of combination in the same molecule provides sufficiently close proximity.

The "promoter" action in this particular case is therefore open to a relatively simple explanation, especially as, when comparison is made between nickel suitably distributed on a support and a copper-nickel preparation on the same support, we have never been able to observe any activity in the latter case beyond that of the standard nickel itself.

Of many tests of the two types of catalyst which we have made under comparable conditions, we may set on record the following, in which in each case one part of total nickel was present per 1,000 of cotton-seed oil hydrogenated.

After one hour's treatment with the plain nickel catalyst, the melting-point of the cotton-seed oil was 52½° C.; with two of the most active copper-nickel catalysts which we have prepared, the melting-points of the oil after treatment were 49° and 46° C. In these experiments, the test was made by taking the copper-nickel catalyst after a preliminary three hours' reduction under cotton-seed oil and employing it in a fresh quantity of the oil; to render the test comparable, our standard nickel catalyst was treated with cotton-seed oil for a similar period under the same conditions before being tested on the oil as above described.

In thus accounting for the "promoting" action of copper-nickel catalyst we do not suggest that all cases of promoter action by the addition of small quantities of various substances to catalysts are to be similarly, or equally simply, explained.

As we have stated previously, however, we are of opinion that a thorough study of individual and specific cases in which catalysts are stimulated is the best prelude to a subsequent generalised theory.